Localization of excess electrons in deformable media

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A theory which describes behaviour of excess electrons in a liquid-like medium is reviewed. The nature of the electronic states and the phenomena of localizations are discussed.

1. Introduction

Excess electrons in deformable media exhibit a variety of phenomena. In low density gases, for example, the electron behaves almost like a free particle. As the gas density is increased, a variety of effects can substantially change the bare state of the electron. At liquid densities the electron may get trapped in a cavity or droplet of solvent particles created by its own field or remains quasi-free depending upon the nature of the electron-solvent interactions. Observed properties such as the electron mobility and absorption spectra probe the nature of the electronic states in deformable materials and the phenomena of localization.

When an electron is solvated in a polar liquid such as water or ammonia, the strong anisotropic electron-solvent interaction causes significant local modification of the equilibrium fluid structure. The electron becomes localized in a small cavity because molecules in a solvation shell orient to create a potential minimum. Even simple fluids are found to exhibit electron mobilities that change by many orders of magnitude as the density of the fluid is altered. In supercritical helium, for example, the electron mobility drops by over 4 orders of magnitude as the fluid density is increased. The reason for this behaviour is strong repulsion between electron and solvent which results in the depletion of the solvent molecules from the region of the electron and forms a highly localized state for the electron. In both cases of localization, the electron adiabatically follows the slow changes in the deformation and therefore feels the instantaneous potential well, and maintains the stationary nature of the well and of the corresponding deformation of the medium with its field.

In many other nonpolar fluids like Ar, CH₄, etc., the electron always remains in a state of high mobility (or quasi-free). The electronic mobility of these fluids is comparable to those found in many semiconducting materials. An interesting density dependence of the mobility has, however, been observed in them. It shows a minimum near critical fluid density and a maximum at liquid density. Even more curiously, Ar, Kr and Xe all display electron mobility maxima at approximately the same number density.

Huang and Freeman have measured the zero field electron mobility in fluid xenon along the liquid-vapour coexistence curve. For densities less than 0.02\( a^{-3}\) (\(a\) being diameter of the atom) they find that the product of the mobility and the number density \(\mu \rho\) is independent of density indicating that under these conditions the mean free path of the electron between collisions with solvent atoms is long compared with the electron thermal wavelength. As the density is increased between \(\rho_s^* = 0.02\) and \(\rho_s^* = 0.2\) (\(\rho_s^* = \rho_{a}^2\)), \(\mu \rho\) gradually decreases, reaching its minimum value at \(\rho_s^* = 0.2\). Increasing the density further causes \(\mu \rho\) to increase dramatically by nearly four times, and it has a maximum at \(\rho_s^* = 0.8\). Finally \(\mu \rho\) decreases by about a factor of 3 from the maximum value as the density is increased to \(\rho_s^* = 1.0\).

Electronic states in reduced dimensions are also of considerable interest. For example, for a system of less than two spatial dimension, electrons are localized with an infinitesimal amount of disorder. The interest in problems of electron or phonon propagation in a one-dimensional (1d) random potential stems from the discovery and extensive experimental study of a certain class of organic or metallo-organic materials. These materials exhibit strongly anisotropic quasi-one
dimensional behaviour attributed to the fact that they consist of long chains weakly interacting with each other. In many of these, the presence of a random potential has been proposed in order to explain their behaviour.

There is in fact a broad range of problems in condensed matter physics (e.g. charge transfer kinetics in biological reactions, metal-insulator transition in fluids, polaron, phonon-assisted hopping of charge carriers in semiconductors and insulators, quantum-tunneling, etc.) which are intimately related to the problem of the solvated electron. Its understanding is therefore related to both scientific and technological advancement of knowledge.

Though the problem of excess electrons in fluids belongs to a general problem of electrons in disordered materials, the liquid medium is in many ways different from solid medium. In liquids, the constituent particles are not only free to relax but they can also diffuse and the local environment around the solute electron can be substantially different from that in a solid. The response of the medium to the presence of the electron must be considered self-consistently as opposed to frozen solid disorder.

Since the quasifree electron is in the conduction band of the solvent, while the bound electron is in a localized state, these two types of electrons have been treated in different ways. For example, Springett et al.\(^\text{18}\) have obtained a theory for the quasifree electron by employing spherical Wigner-Seitz cells each with the size of the volume per particle and centred around a solvent particle. Then, to construct the electron wave-function, periodic boundary conditions are assumed. For the bound electron, on the other hand, they construct a spherical potential well for the electron with the walls of the potential being determined from the average cavity size in the solvent. The free energy for these type of electrons is then compared and that with the lower value is assumed to be the dominant or preferred species.

Based on which state is dominant, different models have been proposed to calculate the mobility of the electron. For the quasifree electron, where the electron is thought to travel through fluid with relative ease, the self-diffusion constant is determined by scattering off the fluid fluctuations. Such a deformation potential theory of Basak and Cohen\(^\text{19}\) seems to give a good qualitative description for the electron mobility in simple fluids except near the critical point, where the isothermal compressibility, and thus the extent of fluid fluctuations, tend to infinity. Attempts have also been made to account for the critical fluctuations and thus to calculate the behaviour of excess electrons in fluids near the critical point.\(^\text{20}\) When the electron is bound, however, the self-diffusion is modelled as being either a ball of some given size diffusing in the solvent, or as a percolation problem of an electron hopping from one favourable site to another.\(^\text{21}\)

Our theory\(^\text{22}\) of the solvated electron which we briefly review in this article is distinct from these other approaches in that the role of solvent fluctuations is determined self-consistently for both the extended and localized electrons. Rather than grafting different pictures of the solvated electron we are able to treat extended and self trapped electrons within a single perspective. We describe the electron in the Feynman path integral formalism.\(^\text{29}\) The electron in this formulation is viewed as a closed polymer. We elucidate this isomorphism in Sec. 2. We integrate out the solvent using liquid state theory. This provides the solvent induced interactions or influence functional for the polymer. The remaining functional integration over the electron polymer paths is done using a variational approach developed by Feynman.\(^\text{24}\)

2. Systematics of Chandler, Singh and Richardson theory

We consider the motion of an excess electron added to an insulating atomic fluid. The Hamiltonian of the system is

\[
H = \frac{p^2}{2m} + V_{es}(r,\{R\}) + \sum_{i=1}^{N} \frac{p_i^2}{2M} + V_{ss}(\{R\}) \quad (2.1)
\]

with

\[
V_{es}(r,\{R\}) = \sum_{i=1}^{N} u_{es}(|r - R_i|) \quad (2.2a)
\]

\[
V_{ss}(\{R\}) = \sum_{1 \leq i < j \leq N} u_{ss}(|R_i - R_j|) \quad (2.2b)
\]

where \(p\) and \(r\) are the excess electron momentum and position vectors, respectively, \(R_i\) and \(P_i\) denote, respectively, the position and momentum of \(i\)th fluid atom, \(N\) the number of atoms and \(u_{es}(r)\) and \(u_{ss}(r)\) are, respectively, the electron-atom and atom-atom interactions. For the sake of simplicity we have taken solvent to be one component fluid of atoms or spherical molecules and assume that the electrons inside each solvent particle satisfy a closed shell structure. Generalization to multi-component system and to solvent of nonspherical molecules is straightforward.

The electron-atom interaction in real system has strong repulsion at short-range due to
orthogonality requirement between the wave functions of the core electrons in the fluid atoms and that of the excess electron and an attraction at large distances. The latter contribution is due to polarization of electron cloud in atoms. The medium polarization may give rise to many-body effect.

In the CSR theory\textsuperscript{22} the excess electron is mapped, using the discretized version of the path integral formulation of the quantum mechanics\textsuperscript{22,23}, on a polymer of \( P \) interaction sites or beads. Thus the partition function of a system of an excess electron and fluid becomes isomorphic to that of a Gaussian polymer with \( P \) monomers and the fluid. In fact, the two different problems of the condensed matter physics are not only unified mathematically in this formulation, but leads to similar physical behaviour. For example, the extended to collapsed state transition in a polymer chain in a solution is analogous to the delocalized to localized states transition for the excess electron.

\section*{A. Isomorphism}

Let us first consider the case of a single electron in an external potential \( \phi(r) \). The partition function for such a system is

\[ Z = \text{Tr} \exp \left( -\beta \hat{H} \right) \] \hspace{1cm} (2.3)

where \( \hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + \phi(r) \)

and

\[ \beta = (k_B T)^{-1} \]

where \( k_B \) is the Boltzmann constant and \( T \) temperature. Eq. (2.3) can be rewritten as

\[ Z = \text{Tr} \left[ \exp \left( -\left( -\frac{\beta}{\hbar^2} \right) \nabla^2 + \phi(r) \right) \right]^P \] \hspace{1cm} (2.4)

Inserting \( P \) complete sets of states, Eq. (2.4) becomes

\[ Z = \int \text{d}r_1 \cdots \text{d}r_P \left| \left| r_1 \right| e^{-\beta \phi(r)} \right| r_2 \left| \left| r_2 \right| e^{-\beta \phi(r)} \right| r_3 \cdots \left| \left| r_{P-1} \right| e^{-\beta \phi(r)} \right| r_1 \rightangle \] \hspace{1cm} (2.5)

In a high temperature expansion (i.e. \( \beta/P \rightarrow 0 \)) one gets\textsuperscript{23,25}

\[ \langle r_i | e^{-\beta \phi(r)} | r_j \rangle = \rho_0 \left( r_i r_j \frac{\beta}{P} \right) \]

\[ \times \exp \left[ -\beta \left( \phi(r_i) + \phi(r_j) \right) \right] \] \hspace{1cm} (2.6)

where \( \rho_0(r_i, r_j; \beta/P) \) is the free particle density matrix relative to the inverse temperature \( \beta/P \);

\[ \rho_0(r_i, r_j; \beta/P) = \left( \frac{Pm}{2\pi \beta \hbar^2} \right)^d \exp \left[ -\frac{P}{2\beta \hbar^2} (r_i - r_j)^2 \right] \] \hspace{1cm} (2.7)

where \( d \) is dimensionality of space. A length

\[ \lambda_e = (\beta \hbar^2/m)^{1/2} \]

describes the uncertainty spreading or equivalently, thermal wavelength associated with a particle of mass \( m \). Inserting Eq. (2.6) into Eq. (2.5) one finds for \( Z \) the approximate expression

\[ Z = Z_p = \left[ \frac{P}{2\pi \lambda_e^2} \right]^{3/2} \int \text{d}r_1 \cdots \text{d}r_P \]

\[ \times \exp \left[ -\beta \omega(r_1, \cdots, r_P) \right] \] \hspace{1cm} (2.8)

where

\[ \omega(r_1, \cdots, r_P) = \sum_{i=1}^P \left[ \frac{P}{2\beta \lambda_e^2} (r_i - r_{i+1})^2 + \frac{1}{P} \phi(r_i) \right] \] \hspace{1cm} (2.9)

with \( r_{P+1} = r_1 \). This periodic condition reflects the fact that the trace has to be taken in evaluating \( Z \).

Equations (2.8) and (2.9) establish an isomorphism between the original quantum problem and the classical problem of a flexible closed chain polymer or necklace. Each point on the necklace interacts with its first neighbours in the chain through a harmonic potential of spring constant \( P/(\beta \lambda_e^2) \) and with the external potential \( \phi(r)/P \). The configuration space spanned by the \( P \) classical particles is the space spanned by a quantum particle obeying the uncertainty principle. As the mass \( m \) gets large the uncertainty (or \( \lambda_e \)) diminishes. The value of \( P \) depends on this uncertainty.

In our problem of interest, the source of the external potential \( \phi(r) \) is the electron-fluid atom interaction. This potential is found to be

\[ \exp \left[ -\frac{\beta}{P} \sum_{a=1}^N \phi(r_a) \right] = \frac{1}{Q_s} \int \text{d}R_1 \cdots \text{d}R_N \]

\[ \exp \left[ -\frac{\beta}{P} \sum_{a=1}^N \sum_{i=1}^N u_{es}(\| R_a - R_i \|) \right] \]

\[ \times \exp \left[ -\beta \sum_{1 \leq i < j}^N u_{ss}(\| R_i - R_j \|) \right] \] \hspace{1cm} (2.10)
where

$$Q_s = \int dR_1 \cdots dR_N \exp \left[ -\beta \sum_{i \neq j}^N u_{ij}(|R_i - R_j|) \right]$$

is the configurational integral for the solvent. Equation (2.10) represents the Boltzmann factor of the solvent interaction averaged over all possible configurations of the solvent. Combining Eqs (2.8)-(2.10) we get the following expansion for the partition function of the electron in the fluid:

$$Z = \left( \frac{P}{2\pi \lambda^2} \right)^{\frac{3N}{2}} \int d\mathbf{r}_1 \cdots d\mathbf{r}_P$$

$$\times \exp \left[ -\beta \sum_{\alpha=1}^P \frac{P}{2\lambda^2} (\mathbf{r}_i - \mathbf{r}_{i+1})^2 \right]$$

$$\times \left( \frac{1}{Q_s} \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \right) \times \exp \left[ -\beta \sum_{\alpha=1}^P \sum_{i=1}^N u_{\alpha i}(|\mathbf{r}_\alpha - \mathbf{r}_i|) \right]$$

$$\times \exp \left[ -\beta \sum_{i \neq j}^N u_{ij}(|\mathbf{R}_i - \mathbf{R}_j|) \right]$$

$$\cdots (2.11)$$

A picture of the classical isomorphic system is shown in Fig. 1, and on viewing the figure, we are led to anticipate the nature of the effect the fluid particles will have on the polymer. Due to the packing interactions, the solvent will tend to compress the polymer. The more confined the structure is, however, the lower is its entropy. Therefore, the compression of the polymer will compete with the entropic preference for an expanded structure. In the isomorphism unfavourable entropy in the classical polymer corresponds to high kinetic energy of the quantal particle. At high enough fluid densities, however, the packing effects dominate, and the solvent will localize the electron polymer. The transition from a relatively diffuse Gaussian polymer (the delocalized states) does not occur in a singular fashion, however, as the size of the (electron) polymer is finite for all nonzero temperatures. Without a phase transition in the solvent (excluded from our consideration herein), and at finite $\beta$, $Z$ will be an analytic function of all relevant parameters, and the change from delocalized to localized states of the electron will not be sudden in the sense of a phase transition. Such a behaviour is approached only in the limit $\beta \to \infty$.

This point can be augmented by citing some relevant length scales. At $T = 1000K$, for example, the distance across the unperturbed electron polymer is roughly $\lambda_c = 25\text{Å}$. This length should be compared with the typical size of a simple liquid molecule, $\sigma_c \approx 5\text{Å}$. The disparity is large, but not so large to imagine that solvent-induced changes will be singular. Another point is also clear. The size of the polymer is not so large that molecular details of the solvent can be ignored. Thus, except at very low temperatures, where a phase transition might be anticipated, the behaviour of the solvated electron is, to some extent, system specific and nonuniversal.

With the isomorphism, the behaviour of a solvated electron can be studied by classical simulation techniques. The closed shell atoms or ions in the liquid solvent may be treated as structureless classical particles ($P = 1$), with these solvent particles coupling the electron via electron-atom pseudopotentials. Such a model is reasonable provided the excitation energies for electrons within an atom are large compared to the energy of the solvated electron. That separation in energy scales corresponding to a separation in time scales too, allows one to integrate out intra-atomic fluctuations before considering explicitly the single excess electron. The determination of electron-atom pseudopotentials can be accomplished by quantum classical electronic structure calculation or by fitting parameterized potentials to empirical properties such as scattering cross-sections and ionization potentials.

By using the isomorphism and this type of model, Parrinello and Rahman studied an electron in molten $K^+\text{Cl}^-$ at $T = 1000K$ with molecular dynamics (MD). For the electron polymer in this system, they found that $P = 200$ was sufficient...
to accurately approximate the continuum limit $P \to \infty$. The molten salt ions were treated classically. Their MD trajectory shows that termination of a localized electron—a small polaron. Coker, Berne and Thirumolai adopted path-integral Monte Carlo simulation for an excess electron dissolved in 6-12 Lennard-Jones fluid. One of their goals was to understand the different experimental behaviours of excess electrons solvated in helium and xenon, respectively. Behaviour of excess electrons in polar solvents has been simulated by many workers.

B. Solvent-induced potential surface for the electron

When integrations are performed over variables $[R_i]$ with the electron (or the isomorphic polymer) coordinates held fixed, Eq. (2.11) reduces to (written in continuum limit, i.e. $P \to \infty$),

$$Z = \int d\mathbf{r} K(r, r', \beta \hbar)$$

where

$$K(r, r', \beta \hbar) = \int d\mathbf{r} \exp\{-S[r(u)]\}$$

with

$$S[r(u)] = \frac{1}{\hbar} \int_0^{\beta \hbar} \frac{1}{2} m |\dot{\mathbf{r}}(u)|^2 + \beta \Delta \mu [r(u)]$$

Here $r(u)$ denotes a path for electron in the imaginary time interval $0 \leq u \leq \beta \hbar$. $\Delta \mu [r(u)]$ is the solvent induced self-interaction for the electron

$$- \beta \Delta \mu [r(u)] = \rho_s \int_0^1 d\lambda \hat{c}_{es}(0, \lambda \rho_s)$$

$$- \frac{1}{2} (\beta \hbar)^{-2} \int_0^{\beta \hbar} du \int_0^{\beta \hbar} du'$$

$$\times v[|r(u) - r(u')|]$$

where

$$\hat{c}_{es}(0, \lambda \rho_s) = \int d\mathbf{r} c_{es}(r, \lambda \rho_s)$$

and

$$v[|r(u) - r(u')|] = - \int d\mathbf{r}' \int d\mathbf{r}'' c_{es}(r', u) x_{ss}(|r' - r''|) c_{es}(r'' - r'')$$

$$\times c_{es}(|r'' - r| u')$$

Here $r$ and $u$ appear as independent coordinates, $r$ is the distance between two sites and $u$ measures the length along the contour of the polymer and

$$x_{ss}(r, r') = \rho_s \delta(r - r') + \rho_s^2 h_{ss}(r, r')$$

is the density-density correlation function of unperturbed fluid. In Eqs (2.15) and (2.16) $c_{es}$ is the electron-solvent direct pair correlation function. Its values are determined from the equation

$$h_{es}(r) = \int d\mathbf{r} \int d\mathbf{r}' \omega(|r - r'|) c_{es}(|r' - r''|) x_{ss}(r'')$$

where

$$\omega(|r - r'|) = (\beta \hbar)^{-1} \int_0^{\beta \hbar} d(u - u') \omega(r - r'; u - u')$$

is the mean intrapolymer correlation function, and $h_{es}(r) = g_{es}(r) - 1$ is the $\epsilon$-solvent pair correlation function.

Note that the self-interaction on the electron path arises because the $\epsilon$ at time slice $u$ couples to the solvent thorough an effective interaction $c_{es}(r, \beta \hbar)$ at a point in the space, then through spatial correlations the solvent can indirectly couple slice $u$ with slice $u'$ provided $u'$ is not farther away in space than a solvent correlation length from $u$. The functions $\omega(r, u - u')$ and $g_{es}(r)$ are defined as

$$\omega(r, u - u') = \langle \delta(|r(u) - r(u')| - r) \rangle$$

and

$$g_{es}(r) = \rho_s^{-1} \sum_i \delta(|R_i - r(u)| - r)$$

The function $\omega(r, u)$ describes the pair structure of the isomorphic classical polymer and it is the equilibrium response function for the electron. Points on the isomorphic polymer do not, however, correspond to positions of the electrons in real time. From known values of this function the real time correlation functions and dynamic response function can be obtained from the method of analytic continuation discussed in Sec. 3. Since on a ring polymer all sites on the average are equivalent, the site dependence disappear from Eq. (2.18), and only the zero frequency component $\omega(r)$ of the equilibrium response function is needed. $g_{es}(r)$ defined by Eq. (2.20b) describes the packing of fluid particles around the electron.
For a given $\omega(r)$, Eq. (2.18) is solved using a suitable closure relation. A standard closure

$$g_{en}(r) = 1 + h_{en}(r) = 0, \quad r < \sigma_{en}$$
$$c_{en}(r) = 0, \quad r > \sigma_{en} \quad (2.21)$$

is suitable for the hard sphere $\varepsilon$-solvent pseudopotential. For a general $\varepsilon$-solvent pseudopotential one may choose a closure similar to the HNC approximation of simple fluids. Equations (2.18) and (2.21) are solved in the following way: The function $c_{en}(r)$ is constructed and adjusted numerically until it is found that $g_{en}(r)$ computed from Eq. (2.18) is zero for $r < \sigma_{en}$. The adjustment determines $c_{en}(r)$ for $r < \sigma_{en}$ and Eq. (2.21) says it is zero for $r > \sigma_{en}$. This solution yields

$$c_{en}(r) = c_{en}(r, \omega(r))$$

That is, the polymer-solvent coupling depends on average polymer pair structure. Nonlinear effects are therefore treated in this model with self-consistent mean pair correlation.

It is to be noted that getting rid of fluid variables (or fields) has effectively given the electron a self-interaction that is nonlocal in (imaginary) time. The partition function is the sum of diagonal elements of the density matrix defined by Eq. (2.13). The diagonal elements are found by putting the boundary condition $r(o) = r(\beta \hbar)$. Thus

$$Z = e^{-\beta F} = \int \int Dr(u) s^{(0)}[r(u)] y[r(u)] \quad (2.22)$$

where

$$y[r(u)] = \exp[-\beta A_{\mu}[r(u)]] \quad (2.23)$$

is the Boltzmann factor of the solvent induced potential surface and

$$s^{(0)}[r(u)] \propto \exp \left[ -\frac{1}{\hbar} \int_{0}^{\beta \hbar} du \frac{1}{2} m |\dot{r}(u)|^2 \right] \quad (2.24)$$

The path integral in Eq. (2.22) corresponds to a single polymer partition function. Incidentally, all the ideas developed here for the isomorphic polymer can be applied to real polymer chain.

C. Variational method

Since the solvent generated interactions are not in general harmonic, Eq. (2.13) or Eq. (2.22) cannot be evaluated in closed form. One, therefore, obtains the density matrix within first cumulant approximation. In this scheme one chooses a trial action $S_0$ for which the exact propagator $K_0$ is known. The exact propagator $K$ is then expressed as

$$K(r', r, \beta \hbar) = K_0(r', r, \beta \hbar) \exp[-(S - S_0)]_{\hbar}$$

where

$$K_0(r', r, \beta \hbar) = \int \int Dr(u) e^{-S_0[r(u)]}$$

In the first cumulant approximation

$$K(r', r, \beta \hbar) = K_0(r', r, \beta \hbar) \exp[-(S - S_0)]_{\hbar} \quad (2.25)$$

Thus, we observe that within first cumulant approximation the task of obtaining the density matrix reduces to that of obtaining $K_0$ and $(S - S_0)_{\hbar}$. The choice of $S_0$ is arbitrary to the extent that $K_0$ is exactly known. This consideration leads us to $S_0$ as a two time quadratic action of the form

$$S_0 = \frac{1}{2} m \beta \int_{0}^{\beta \hbar} du \frac{1}{\beta \hbar} |\dot{r}(u)|^2 + \frac{1}{2} \int_{0}^{\beta \hbar} du \int_{0}^{\beta \hbar} du' \beta \hbar \times y(u-u') r(u) \cdot r(u') \quad (2.26)$$

Since we are concerned here with closed paths, $r(0) = r(\beta \hbar) = r$, we represent the path as

$$r(u) = \sum_{n} a_n e^{i \Omega_n, u} + c \cdot c$$

and

$$y(u-u') = \sum_{n} \gamma_n e^{i \Omega_n(u-u')} \quad (2.27)$$

where $\Omega_n = \frac{2 \pi n}{\beta \hbar}$

Thus the path integral over $r(u)$ can be converted into multiple integrals over $a_n$ leading to the following expression for $K_0$.

$$K_0(r', r, \beta \hbar) = (2 \pi \lambda n^2)^{-d/2} \left\{ \prod_{n=1}^{\infty} \left( 4 \pi^2 n^2 A_n / \lambda_n^2 \right)^{d/2} \right\}$$

where

$$A_n = (\beta m \Omega_n^2 + \gamma_n)^{-1}$$

Since the first term in Eq. (2.9) is constant and contributes only a constant factor to the density matrix, we drop this term in definition of the action for the excess electron, but include its contribution whenever essential. Thus,

$$S = \frac{1}{2} m \beta \int_{0}^{\beta \hbar} du \frac{1}{\beta \hbar} |\dot{r}(u)|^2 - \frac{1}{2} \beta \hbar \int_{0}^{\beta \hbar} du \int_{0}^{\beta \hbar} du'$$

$$\times y[|r(u) - r(u')|] \quad (2.29)$$
From Eqs (2.26) and (2.29) we get

$$-\langle S - S_0 \rangle_n = \frac{1}{2(\beta \hbar)^2} \int_0^{\tau_n} du \int_0^{\tau_n} du' \times \gamma_n(u - u') \langle r(u) r(u') \rangle_n$$

$$+ \frac{1}{2(\beta \hbar)^2} \int_0^{\tau_n} du \int_0^{\tau_n} du' \int \frac{d^4k}{(2\pi)^4} \nu(k)$$

$$\times \langle \exp[ik(r(u) - r(u'))] \rangle_n \ldots (2.30)$$

where $\nu(k)$ is the Fourier transform of $\nu[r(u) - r(u')]$

From Eq. (2.20) we note that

$$\omega(k, u - u') = \langle \exp[ik(r(u) - r(u'))] \rangle_n$$

is the Fourier transform of the structure of the isomorphic polymer. The evaluation of path integral leads to

$$\omega(k, u - u') = \exp[-2k^2 \sum_{n \neq 1} A_n(1 - \cos \Omega_n(u - u'))] \ldots (2.31)$$

Evaluating all path integrals involved in Eq (2.30) and using Eq. (2.21) we get

$$-\langle S - S_0 \rangle = \frac{1}{2(\beta \hbar)^2} \int_0^{\tau_n} du \int_0^{\tau_n} du' \int \frac{d^4k}{(2\pi)^4} \nu(k)$$

$$\times \omega(k, u - u') \ldots (2.32)$$

Substitution of Eqs (2.28) and (2.32) into Eq. (2.25) gives an expression for the diagonal elements of the density matrix. The functional integration governed by the Euclidean time action yields the correlation function

$$R_2(u) = \langle |r(u) - r(0)|^2 \rangle = 4 \sum_{n \neq 1} \langle |r_n|^2 \rangle (1 - \cos \Omega_n u)$$

where

$$\langle |r_n|^2 \rangle = dA(\Omega_n) \ldots (2.33)$$

The variational parameter $\gamma_n$ is given by

$$\gamma_n = -d(\beta \hbar)^{-1} \int_0^{\tau_n} du (1 - \cos \Omega_n u) \int \frac{d^4k}{(2\pi)^4} k^2$$

$$\times \nu(k) \exp[-k^2 \sum_{n \neq 1} A(\Omega_n)(1 - \cos \Omega_n u)] \ldots (2.34)$$

In the real time domain $\gamma_n / \Omega_n$ is a frequency dependent friction kernal or memory function.

The effective mass of the solvated electron is calculated by introducing a fictitious driving force $f$ acting on the electron in the Hamiltonian. The effective mass is derived from the acceleration rate against the force. The effective mass thus defined has the meaning of inertial mass against the force and is expressed in terms of $\gamma_n$, i.e.

$$\frac{m^*}{m^*} = 24 \sum_{n \geq 1} (4\pi^2 n^2 + \gamma_n \lambda_n^2)^{-1} \ldots (2.36)$$

3. Time dependent properties

Here the extension of the CSR theory to real time domain by the method of analytic continuation is briefly discussed. The idea behind the analytic continuation is straightforward. If one considers an autocorrelation function in the complex time plane, one finds that it is analytic in strips that extend from $-\infty$ to $\infty$. The width of these strips is given by $\lambda_n^2$. Since the function is analytic in these strips, if one is able to calculate the function on the line from $0$ to $-i \lambda_n \beta$ (i.e. if one is able to perform the equilibrium calculations), then there exists a unique analytic continuation into the real time domain. So, having the thermal electron auto-correlation function is sufficient to calculate the electron auto-correlation function in real time. The procedure used by Baym and Mermin is to determine the autocorrelation function at discrete values of the imaginary frequency and extend those formulas to real frequencies. They showed that there exists only one autocorrelation function which satisfies both the requirements: that it is equal to the known values at the discrete imaginary frequencies, and that it tends to zero at both positive and negative infinity.

To do the analytic continuation of Euclidean time correlation function, we replace every occurrence of $\beta \hbar$ with $i \tau$, where $\tau = -i \lambda_n \beta$. So, for example,

$$\Omega_n = \frac{2\pi n}{\beta \hbar} \omega_n = \frac{2\pi n}{\tau} = i\Omega_n$$

$$A(\Omega_n) = (\beta m \Omega_n^2 + \gamma_n)^{-1} \phi(z)$$

$$= -[\beta mz^2 + \gamma(z)]^{-1} \ldots (3.1)$$

$$\xi(t) = \frac{1}{6} \langle |r(t)|^2 \rangle$$

$$= \int_0^\infty \frac{d\omega}{\pi} \phi''(\omega) \beta \hbar \left[ \coth \left( \frac{1}{2} \frac{\beta \hbar \omega}{2} \right) \right.$$

$$\left. \times (1 - \cos \omega t) + i \sin \omega t \right] \ldots (3.2)$$
\[ \dot{\gamma}(\omega) = \left(d^2\beta\hbar\right)^{-1} \int_0^t dt (e^{i\omega t} - 1) \int \frac{2d^d k}{(2\pi)^d} k^2 \times \nu(k) \text{Im}\{\exp[-k^2 \xi_>(t)]\} \]  

\[ \text{(3.3)} \]

where \( \phi''(\omega) \) is the imaginary part of \( \phi(\omega) \), and \( \xi_>(t) \) is analytic continuation of \( R^2(\omega)/6 \) and \( \gamma(\omega) \) is that of Eq. (2.35).

The electron diffusion constant is given as 

\[ \lim_{\omega \to 0} \gamma(\omega) = \frac{D}{\omega} \]

From Eqs (3.1)-(3.3) we have

\[ \frac{1}{D} = \lim_{\omega \to 0} \frac{\dot{\gamma}(\omega)}{i \omega} \]

\[ = \frac{2}{d^2\beta\hbar} \int_0^\infty dt \int \frac{d^d k}{(2\pi)^d} k^2 \nu(k) \times \text{Im}\{\exp[-k^2 \xi_>(t)]\} \]  

\[ \text{(3.4)} \]

Equations (3.2)-(3.4) are solved iteratively to find the value of the diffusion constant.

4. Discussion

The primary physical phenomenon addressed by the CSR theory is the process of localization or self-trapping of the electron. At low densities of the solvent the electron polymer is fairly extended fluctuating with nearly the free particle Gaussian statistics, where the second moment is given by

\[ R^2_{\text{free}}(u-u') = 3 \lambda_e^2 (u-u') (\beta \hbar - u + u') / |\beta \hbar|^2 \]

\[ \text{(4.1)} \]

The overall size of the extended electron is therefore roughly \( \lambda_e \), and under normal conditions, \( \lambda_e \) is much larger than the diameter of a solvent molecule, \( \sigma_e \). At high solvent densities, on the other hand, the packing of the fluid environments may prohibit spatially extended fluctuations and the electron gets localized occupying a region characterized by the length \( \sigma_e \). The electron correlation function \( R(u-u') \) for these two cases have contrasting qualitative behaviour. When there is ground state dominance characteristic of a localized or compact state the function \( R(u-u') \) starts from zero at \( u-u' = 0 \) and rapidly increases to its “saturation” value. The characteristic rise time \( \Delta u \) of this initial (imaginary) time dependence is a measure of the energy difference \( \Delta E \) between the ground state and the first manifold of the excited states.

\[ \Delta E = \hbar / \Delta u \]

This, however, gives only a rough estimate of the excitation energy. For more accurate estimate real-time methods are necessary.

A measure of the relative delocalization of the electron is found from the quantity

\[ s = 2R \left( \frac{1}{2} \beta \hbar \right) / \sqrt{d \lambda_e^2} \]

\[ \text{(4.2)} \]

which measures the relative size of the electron. The behaviour of the excess electron is found to depend sensitively on \( \lambda_e, \rho_e \) and on the electron-solvent atom pseudopotential.

Recently Sethia and Singh considered a bath of hard rods of length \( \sigma_e \) distributed in one dimension. The density-density correlation function \( \chi_{ss}(r) \) is found exactly. For the electron-atom interaction they considered two models. In the first model, the interaction is taken to be hard rods with characteristic length \( \sigma_e \), defined as

\[ u_e(x) = \infty ; \quad x < \sigma_e \]

\[ = 0 ; \quad x > \sigma_e \]

\( \sigma_e \) was taken to be equal to \( 1/2 \sigma_e \). In the second model a negative \( \delta \)-function potential is situated at the centre of each hard rod,

\[ u_e(x) = -V_0 \delta(x-X_n) \]

\[ \text{(4.4)} \]

where \( V_0 > 0 \) and \( X_n \) is the position of the nth ion. An isolated potential of this form leads to a bound state at the energy \( E_0 = -1/4V_0 \). Result for this model is given in terms of a dimensionless parameter

\[ \epsilon = \frac{\rho_e \hbar^2}{m V_0} = \frac{\rho_e^* (\lambda_e / \sigma_e)^2}{\beta(V_0 / \sigma_e)} \]

\[ \text{(4.5)} \]

which measures the density relative to the potential strength.

Since the interaction sites in the first model are excluded from penetrating spheres of radius \( \sigma_e \) surrounding each particle, an electron is always localized between two adjacent scatterers. The localization length is function of the density of the solvent and the temperature (see Fig. 2). The electron-solvent pair correlation shown in Fig. 3 for \( \lambda_e / \sigma_e = 4 \) has some interesting features: First, we note that the electron paths tend to expel solvent particles from the vicinity of the electron and form a cavity in which it gets trapped. The size of the cavity can be estimated from the figure. The localized electron exerts a field to create local freezing in solvent at higher densities. A contrasting behaviour was found for the second model. For the force parameters taken by Sethia and
Fig. 2—Reduced localization length of an electron in the one-dimensional fluid of hard rods for the primitive model as a function of solvent density at $\lambda_e = 4\sigma$ (see ref. 37).

Fig. 3—The electron-solvent radial distribution function at $\lambda_e = 4\sigma$ and several solvent densities for the primitive model of an electron in a fluid of hard rods (see ref. 37).

Fig. 4—Reduced correlation length of an electron in one-dimensional fluid of hard rods as a function of solvent density at $\epsilon = 1$ for the $\delta$-potential model (see ref. 37).

Fig. 5—The electron-solvent radial distribution function at several solvent densities for the $\delta$-potential model at $\epsilon = 1$ (see ref. 37).

Singh, the electron is found to exist in a 'quasi-free' state and forms a cluster of solvent particles around it. Ordered structure is found to develop in the cluster as the solvent density is increased. These features are shown in Figs 4 and 5. We note that the both repulsive and attractive parts of electron-solvent pseudopotential separately lead to localization of the electron by creating a cavity and forming a cluster of the fluid atoms around it, respectively. The same behaviour is expected to take place in the case of three dimensional system.

For a case of three-dimensional system,\textsuperscript{34,38-40} most of reported results are for a fluid of hard spheres interacting via a pair potential,

$$u_e(r) = \begin{cases} \infty ; & r \leq \sigma_e \\ 0 ; & r > \sigma_e \end{cases} \ldots (4.6)$$

and for $\tilde{e}$-solvent atom pseudopotential written as

$$u_{es}(r) = \begin{cases} \infty ; & r \leq \sigma_{es} \\ 0 ; & r \geq \sigma_{es} \end{cases} \ldots (4.7)$$

with $\sigma_{es}/\sigma_e$ ranging between 0.15 to 0.7.

The electron localization depends on the value of $\sigma_{es}/\sigma_e$. If its value is small say $= 0.15$ the electron is found to be in delocalized states at all finite temperatures having very weak tendency of localization around $\rho_s = 0.6$. For the intermediate values of this quantity (i.e. $\sigma_{es}/\sigma_e = 0.3$), the electron exhibits a rather sharp transition from delo-
calized to localized states as the temperature is lowered and the solvent density is increased. The transition temperature is found to be nonmonotonic function of the solvent density. This is shown in Fig. 6 in which $s$ is plotted [defined by Eq. (4.2)] as a function of $\lambda_e/\sigma_s$ for several solvent densities. If the range of the repulsive interaction of $\varepsilon$-solvent pseudopotential is large (i.e. $\sigma_{es}/\sigma_s \geq 0.5$) the electron gets localized at all temperatures as the solvent density is increased. Though the onset of the transition sets in at lower density for larger $\sigma_{es}/\sigma_s$ values, the range for the solvent density over which transition takes place increases with temperature and $\sigma_{es}/\sigma_s$.

The transition is a fluctuation induced transition in much like the polaron formation in harmonic crystals. But here, the effect is due to excluded volume rather than polarization. The electron pushes on the solvent to make space for itself. The larger the space the lower the electron kinetic energy. Large space in a sea of spheres, however, is costly in terms of solvent energy so the solvent pushes back. The strength of this is proportional to the compressibility of the solvent. The balance between the electron kinetic energy and the solvent compressibility results in the stable structure. The localized electron is in cavity with energy spacings larger than $k_B T$-thus the phenomena of ground state dominance. These cavities are sometimes referred to as Lifshitz traps.

In Fig. 7 are shown the results$^{35}$ for the diffusion constant calculated using the formulation of Sec. 3 for system described by interactions given by Eqs (4.6) and (4.7) and $\sigma_{es} = 1/2 \sigma_s$. As the system passes from an extended to a localized or self-trapped state the diffusion constnat drops precipitously. Notice also the switch in temperature dependence. At low solvent densities, increasing temperature (i.e. decreasing values of $\lambda_e$) lowers the diffusion constant. This is metallic behaviour. At high densities, however, the opposite trend is observed. Indeed, to diffuse, electrons must be in excited states, and the population of excited states goes as $\exp(-\beta \Delta E)$ where $\Delta E$ is the energy gap from the ground state. We known a gap exists because the localized equilibrium structure exhibits ground state dominance. Thus, the self trapped state is akin to a semiconductor. The precipitous drop in diffusion constant is much like a phase transition where small changes in external parameters can cause an enormous change in an observed property.

A different behaviour for the excess electron is expected when both the attractive and repulsive parts of the pseudopotential are strong. As has been seen in case of one dimensional system, the repulsive and attractive parts of the potential separately lead to localization of the electron by creating a cavity and forming cluster of the solvent atoms around it, respectively. As a consequence of the two different com-
petitive mechanism of the localization generated due to the repulsive and the attractive parts of the electron-atom interaction we expect to have delocalization at some intermediate range of the fluid density where both interactions become equally important. One may argue that at low fluid densities the excess electron essentially gets affected by the attractive part of the potential and therefore has the tendency to get localized. On the other hand at high fluid densities the electron essentially feels the repulsive part of interactions and has the tendency to repel the atoms from its region of existence. At the intermediate densities both interactions affect the behaviour of the electron and, therefore, mutually cancel each other's effect. This explains the existence of maximum in the mobility of excess electron in most nonpolar fluids. The CSR theory is in effect a self-consistent small amplitude fluctuation theory. It employs variational method to treat effects of the fluctuations in electronic configurations and it estimates the role of density fluctuations in the solvent through the use of Gaussian density functional approximation. In the region of transition from the delocalized to localized state, the fluctuations in the isomorphic polymer chain are not small and it is these fluctuations which enable the chain to sense the disorder which produces localization. It may also be noted that the CSR theory does not include the dynamics of the solvent. A moving electron may drag or repel the solvent from its path and thus create a local motion of the solvent. Electron diffusion may also arise from the diffusion of the solvent molecules surrounding it. The theory should be extended to include these features.

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